A

Synopsis On

DFT Studies on Doped Metal Oxide Nanostructures for Photocatalytic Applications

Submitted by

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to

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1. Origin of the Proposal

The rapid depletion of fossil fuel reserves is one of the threats to human civilization on mother earth with respect to the exponential growth rate of global energy consumption. The global energy consumption presently is about 36 exajoules and by 2050, renewable energy consumption is expected to increase and will reach about 161 exajoules [1]. This scenario has alerted us to look for alternative renewable energy solutions like photovoltaics, wind turbines, solar fuels, biomass conversion catalysts, electrification of automotive vehicles, fuel cells, storage batteries, flow batteries and any other energy conversion technology [2,3]. Amongst these, the optimal utilization of the solar energy enables us to move away from the dependency on fossil fuels owing to the fact that the energy of sunlight strikes on earth in one hour is more than the total consumption of energy in one year at global scale [4]. Of many ways to harvest solar energy, breaking chemical bonds and thereby storing energy in chemical form is prominent [3]. In photo-catalysis, the splitting of water with the help of sunlight into hydrogen and oxygen can be achieved and hence became one of the promising research areas existing today to meet global energy requirements [5-7].

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2. Review of status of Research and Development in the subject

2.1 International Status

In the year 1972, Honda-Fujishima have published a ground breaking study on water splitting to produce hydrogen by using TiO_2 as photoanode material, provided a proof to do photo-electrochemical water splitting [1]. The basic principle is, electrons in valence band (VB) of photoanode material will be jumped to conduction band (CB) while holes remain in VB upon irradiation to the suitable electromagnetic radiation on its surface. Then the holes will move towards the interface of anode and electrolyte to participate in water splitting and produce oxygen. At the same time, electrons move through external circuit to cathode to produce hydrogen. The free energy change in this process ($2H_2O \longrightarrow 2H_2+O_2$) amounts to 4.92 eV for four electron process i.e. each electron-hole needs 1.23 eV of potential difference to the reaction.

Since then, many research efforts have been reported not only to understand the basic mechanism of photocatalytic water splitting but also to improve the efficiency of nontoxic, low cost, stable and environmental friendly TiO_2. The large band gap (~3.0 eV for rutile and ~3.2 eV for anatase) restricts to capture the photons beyond ultraviolet region by loosing visible and long wave length near infra red region which covers more than half of the solar spectrum[2]. Doping is an effective method to tune the VB and CB and extend the absorption edge into visible region further. The doping with non-metal elements shifts VB up whereas CB will be stabilized with transition metal element dopants, in result decreasing the band gap. On the other hand co-doping with both transition metal and non-metal dopants will modify both VB and CB simultaneously [3].

The developments in terms of principles, mechanism and materials application aspects have been well documented time to time [4,5]. In a report, the mechanistic pathway of photocatalytic oxygen evolution on aqueous TiO_2 has been studied through first principle molecular dynamics to understand the reactive intermediates and also suggested that the participation of lattice oxygen in evolution of O_2 in anatase TiO_2 which is not the case in rutile counterpart [6]. The correlation between high surface area to volume ratio and photocatalytic activity has been studied with two-dimensional TiO_2 nanosheets photo and electrochemical oxidation of water along with transition metal doping effect in reducing rate limiting thermodynamic barriers and required overpotentials [7]. On the other hand, adsorption of single metal atoms of Pt, Pd, Rh and Ru on rutile TiO_2 surface has been carried out to understand the work function and surface activities of both doped and undoped anatase TiO_2 (101) surfaces [8]. Wenxian Li has reviewed the doping effect of several transition metals, rear earths, p-block metals and metalloids and non-metal elements as dopants and summarized the theoretical results on dopant induced variation in electronic structure, band gap and density of states of TiO_2 [9]. The prominent role of highly oxidized metal ions as dopants in photocatalytic oxygen evolution has

been explored with experimental results on Mn, Fe, Co, and Ni doped various nano crystals [10]. Apart from this, the splitting of d-orbitals of doped transition metals which causes the reduction of overpotentials and facilitation of oxygen evolution has been experimentally shown in another report [11].

Similarly, many reports on main group elements as dopants in anatase TiO_2 in order to modify the VB are found. Specifically, the elements B, C, N, F and S are most widely studied as dopants to alter the VB, results shifting the band gap from UV range to visible range and improves the hole mobility at the surface [12-16]. On the other hand, the bulk vs surface doping effect of C, N and S on TiO_2 has been thoroughly dealt with both experimentally and theoretically and concluded that the surface or sub-surface doping impacts the electronic structure of TiO_2 and improves the photocatalytic activity [17].

The main disadvantage with monodoping is with respect to the partial occupation of the localized mid-gap states which may facilitate hole-electron pair recombination and thus reduce the photocatalytic activity [18]. To overcome this negative effect, the co-doping procedure is commonly adopted where transition metal ions are used for altering the CB whereas non-metal ions for VB [19-21].

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2.2 National Status

Large number of research groups across India have been found active in photocatalytic water splitting research area on metal oxides, sulfides, carbon based materials, and transition metal complexes. However, outcome of the most of the works published resides mainly in hydrogen evolution reactions. S.M. Senthil Kumar et al have shown that MoS_2 nanospheres with higher defect concentration exhibited excellent hydrogen evolution activity [1]. Similarly, photoelectrocatalytic activity of MoS_2/graphene vertical heterostructures are suggested with negligible potential difference i.e. 0 eV [2]. Reduced graphene oxide-MoS_2 supported $NiCo_2O_4$ photocatalyst has been tested for hydrogen evolution reaction and Rhodamine B dye degration successfully by S. Basu and co-workers [3]. On the other side, transition metal complexes and polymeric materials have also been studied by various research groups for hydrogen evolution [4-7]. Mixed metal oxides and their hetero junction

photoelectrodes were also studied by both experimentally and density functional theory (DFT) for photocatalytic applications for water splitting as well as dye degradation [8-11]. The basic concepts behind improving the visible light responsive metal oxides by doping with metals, non-metals and improving the surface chemistry have been reviewed [12-13]. Apart from this, very few reports are found by research groups from CSIR-NCL, Pune and IIT, Kharagpur for photocatalytic oxygen evolution materials, namely NiCo alloy supported N-doped porous graphene and transition metal doped (Fe, Co, Cu) TiO_2 [14-15].

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2.3 Importance of the proposed project in the context of current status

As per discussion in the previous sections, though there exist great number of experimental results on (co) doping on TiO_2 photoanode material, the number of first principle studies of how dopants affect light absorption, carrier transport and catalytic reactions are limited. On the other hand, the reliability of results based on first principle density functional theory methods has been proven by several reports and also it has reached to prediction kind of studies as well [1]. Moreover, tuning of VB and CB in order to reduce the band gap and minimization of charge carrier recombination are successfully dealt at bulk level DFT calculations, but water splitting mechanism with respect to several dopants has not been well established with the surface of doped TiO_2. To be specific, in case of water splitting to get oxygen evolution at photoanode, several queries are still unanswered like, which parameter influence a dopant to present on surface or sub-surface of TiO_2, the interaction of H_2O and intermediates like -O, -OH, -OOH and -H are preferred to dopant or Ti center, the possibility of formation of new defects and their effect on expected band gap and mixing of dopant orbitals leads to generation of new bands are some of them. Hence, we would like to propose systematic studies on the gaps mentioned above.

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3. Work Plan

3.1 Methodology

As mentioned in section 2.3, as very few articles are seen with first principle DFT calculations at surface phase in contrast to the bulk phase of TiO_2, the objectives of the present proposal are as follows.

1) Studying the position of each dopant (metal, non-metal and metalloids) location i.e. it prefers to present on surface/sub-surface or in bulk
2) Understanding the interaction between H_2O and TiO_2 surface along with the reaction intermediates like –OH, –OOH and –O
3) Studying the effect of newly formed structural defects with doping
4) Studying the changes in band structure with mono and co-doping (metal and non-metal ions)
5) Doping of metalloids to avoid mixing of d-orbitals in the forbidden region of band gap.

All the geometries will be fully optimized with Vienna *Ab initio* Simulation Package (VASP) using the projector augmented wave (PAW) method with the generalized gradient approximation and "Hubbard U" scheme for a better treatment of the valence electrons of metal ions. A suitable plane-wave cutoff energy will be employed to control the fineness of this mesh. All oxygen evolution reaction steps will be investigated using fully optimized structures in which lattice vectors and ionic positions are fully relaxed until the maximum atomic forces are less than optimal value.

Using well-established structures, the catalytic activities of doped TiO_2 surfaces will be calculated by sequentially calculating the Gibbs free energies for the elementary steps based on the following mechanism.

During the electrochemical water splitting by using solar radiation, photons excite electrons in a semiconductor in which the energy level of the VB is sufficiently low to CB. This process involves with the substantial overpotential and energy losses at anode where oxygen is evolved. This reaction can be represented with the following 4 electron transfer model [equation 1].

$$2H_2O(l) + 4X1.23\ eV \rightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

This proposed reaction mechanism consists of four consecutive proton and electron transfer steps where HO*, O* and HOO* are found to be reaction intermediates [equations 2-5].

$$OH^- + * \longrightarrow OH^* + e^- \quad (2)$$

$$OH^* + OH^- \longrightarrow O^* + H_2O(l) + e^- \quad (3)$$

$$O^* + OH^- \longrightarrow OOH^* + e^- \quad (4)$$

$$OOH^* + OH^- \longrightarrow * + O_2(g) + H_2O(l) + e^- \quad (5)$$

where * represents an active site on TiO_2 surface, (l) and (g) refer to liquid and gas phases respectively, and O*, OH* and OOH* are absorbed intermediates.

The binding energies of the intermediates O*, OH* and OOH* on the TiO_2 surface (doped and undoped) will be obtained to know the rate limiting step in the overall reaction, on various active sites for different structures, as follows.

$$\Delta E_{OH^*} = E(OH^*) - E(*) - (EH_2O - \frac{1}{2}EH_2) \quad (6)$$

$$\Delta E_{OOH^*} = E(OOH^*) - E(*) - (2EH_2O - \frac{2}{3}EH_2) \quad (7)$$

$$\Delta E_{O^*} = E(O^*) - E(*) - (E_{H_2O} - EH_2) \quad (8)$$

where E(*), E(OH*) and E(OOH*) are the ground state energies of the clean surface and surfaces adsorbed with OH*, O* and OOH* respectively. E_{H2O} and E_{H2} are the calculated DFT energies of H_2O and H_2 molecules in the gas phase.

Additionally, the zero-point energy and entropy corrections will be considered. From these calculations, the binding free energies like ΔE_{OH^*}, ΔE_{OOH^*} and ΔE_{O^*} could be written in terms of adsorption free energies,ΔG_{ads}, by the following equation

$$\Delta G_{ads} = \Delta E_{ads}^{DFT} + \Delta ZPE - T\Delta S \quad (9)$$

where, T is the temperature and ΔS is the entropy change.

The free energy diagram will be constructed considering the following four electron reaction paths

$$\Delta G_{1=}\Delta G_{OH*} + \mu_{e-} - \Delta G_{OH-} - \Delta G_{*} \quad (10)$$

$$\Delta G_{2=}\Delta G_{O*} + \Delta G_{H_2O} + \mu_{e-} - \Delta G_{OH*} - \Delta G_{OH-} \quad (11)$$

$$\Delta G_{3=}\Delta G_{OOH*} + \mu_{e-} - \Delta G_{O*} - \Delta G_{OH-} \quad (12)$$

$$\Delta G_{4=}\Delta G_{O_2} + \Delta G_{H_2O} + \mu_{e-} - \Delta G_{OOH*} - \Delta G_{OH-} - \Delta G_{*} \quad (13)$$

From the free energy diagram, an important parameter for electrocatalytic activity will be estimated that is the magnitude of the potential-determining step in four consecutive proton and electron transfer steps. This is the specific reaction step in the four-step mechanism with the largest ΔG , that is, the concluding step to become downhill in free energy as the potential increased

$$\Delta G = \max[\Delta G_1^0, \Delta G_2^0, \Delta G_3^0, \Delta G_4^0] \quad (14)$$

The theoretical overpotential at standard conditions is then given by

$$\eta = \left[\frac{G}{e}\right] - 1.23 \quad (15)$$

The lower the overpotential then superior the photocatalytic activity of doped photoanode in water splitting reaction.

The quantitative performance of doped system can be calculated by the relative position of η and absorption energy values in the volcano plot i.e. more closer to the peak confirms a better catalyst.

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